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Low-Frequency Isotropic Raman Spectra of Concentrated Aqueous KX (X: Cl, Br, NO_3, and SCN) Solutions

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Polarized Raman spectra for concentrated aqueous KX solutions (X: Cl, Br, NO_3, and SCN) were measured in the frequency range of $30 \leq \tilde{\nu} \leq 1000\,\mathrm{cm}^{-1}$ in order to find the totally symmetric stretching vibrational mode of hydrated K^+. The observed polarized peak intensities of the intermolecular vibrational mode at $\tilde{\nu} = 160$–$180\,\mathrm{cm}^{-1}$ in the isotropic spectra for KCl and KBr solutions exhibit systematic increase with increasing solute content. Polarized components at $\tilde{\nu} = 166$ and $167\,\mathrm{cm}^{-1}$ were observed in the isotropic spectra for 5 mol % KNO_3 and 7 mol % KSCN solutions, respectively. The position of these polarized peaks were found to shift to lower frequency by 7–15 cm^{-1} in D_2O solutions, which is consistent with the expected value of the H/D isotopic shift calculated for the totally symmetric vibrational mode of the hydrated K^+, $K^+(H_2O)_6$.

The hydration structure of K^+ has long been a matter of interest because of its significant importance in wide fields of chemical and biological sciences. Earlier X-ray diffraction study by Brady revealed that the hydration number of K^+ is 4.[1,2] Results of more recent X-ray diffraction studies by Pálinkás et al.[3] and by Ohtaki and Fukushima[4] indicated that the nearest neighbor $K^+\cdots H_2O$ distance is $r(K^+\cdots H_2O) = 2.80$[3] and 2.81(1)[4] Å with the coordination number of 6[3] and 5.8(1),[4] respectively. On the other hand, the distribution function around the K^+, $G_K(r)$, obtained from neutron diffraction experiments by $^{39}K/^{41}K$ isotopic substitution, exhibits much broadened distribution of water molecules in the first hydration shell of K^+.[5] Ohtomo and Arakawa reported that $r(K^+\cdots O_W) = 2.7(1)$ Å and $n(K^+\cdots O_W) = 8$, (O_W: water oxygen atom) from the difference interference function $\Delta S_m(Q)$ between observed neutron structure factors for 1 M KCl–D_2O solution and that for pure D_2O.[6] A combined analysis of the X-ray and neutron diffraction data for aqueous 7 mol % KCl solution in the null water indicated that the nearest neighbor $K^+\cdots O_W$ distance is 2.80(1) Å with the coordination number of 6.2(1).[7] Results of more recent neutron diffraction studies with H/D isotopic substitution combined with EPSR analysis showed that $r(K^+\cdots O_W) = 2.65$ Å and $n(K^+\cdots O_W) = 5.6$–6.4.[8–10] This $K^+\cdots O_W$ distance seems somewhat shorter than the sum of effective ionic radii of K^+ of octahedral coordination (1.37 Å)[11] and the effective radius of water molecule in the aqueous solution (1.39 Å).[12] On the other hand, much smaller hydration number of K^+, $n(K^+\cdots H_2O) = 3.0$, was proposed by NMR.[13] The value of the hydration number obtained from NMR may be regarded as the number of water molecules strongly bound to the neighboring ion. Moreover, considerably short residence time of the water molecule in the first hydration shell of K^+, 4.8[14]–9.4 ps,[15] estimated from the molecular dynamics (MD) simulation studies, could prevent determining reliable hydration number by NMR. An earlier ab initio study on the isolated $K^+(H_2O)_n$ cluster represented that the $K^+\cdots O_W$ distance of 2.79 Å in the case of the number of the nearest neighbor water molecules being 6. Classical MD simulation studies revealed that the $K^+\cdots O_W$ distance in the aqueous solutions is 2.76,[14] 2.80,[15] 2.78,[16] and 2.80 Å[17] and corresponding hydration number is 7.5,[14] 7.4,[15] 7.8,[16] and 7.1,[17] respectively. The results of ab initio MD study, $r(K^+\cdots O_W) = 2.81$ Å and $n(K^+\cdots O_W) = 6.75$,[18] agree well with those obtained from classical MD work. Considering that the coordination number obtained from the MD simulation is the integral value of the first peak of the partial pair correlation function, $g_{ij}(r)$, to the first minimum of the $g_{ij}(r)$, which is known to give larger coordination number than that determined from diffraction experiments in which a symmetric Gaussian distribution of the short range interaction is often assumed. The hydration number of the cation can be determined by using a infrared double difference spectroscopic method developed by Lindgren et al.[19–22] The hydration number of K^+ in aqueous 7 mol % KCl solution was determined to be 5.8(1),[7] which is in reasonable agreement with the value 6.2(1) obtained from the combined analysis of X-ray and neutron diffraction data.[7] The concentration dependence of hydration number of K^+ in aqueous HCOOK solutions has been investigated by employing double difference analysis combined with ATR-IR analysis.[23] The hydration number, $n(K^+\cdots OH_2)$, was found to be ca. 6 at concentration below 5 mol % HCOOK. Consequently, values $r(K^+\cdots O_W) = 2.8$ Å and $n(K^+\cdots O_W) = 6$ for the hydration parameters of K^+ are considered to be the most reliable at present.

Assuming a stable structural unit, $K^+(H_2O)_6$, is present in the aqueous solution, the totally symmetric vibrational mode (ν_1) of this structural unit is expected to appear as a polarized peak in the Raman spectra in the low-frequency region. Although the symmetric stretching vibrational mode of the hydrated polyvalent transition-metal ions has been extensively investigated,[24,25] the observation of the ν_1 mode of hydrated

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alkali metal ions has long been considered difficult because of the short residence time of the water molecules in the first hydration shell of the alkali metal ion.[24] Recently, the ν_1 mode of the hydrated Li^+, $Li^+(H_2O)_n$ ($n = 4$ and 6) has been observed in the isotropic Raman spectra at $\tilde{\nu} = 160$–$260\,cm^{-1}$.[26,27] The ν_1 mode of the hydrated Na^+, $Na^+(H_2O)_n$ ($n = 4$, 5), has also been found at $\tilde{\nu} = 183$–$187\,cm^{-1}$ by means of the isotropic Raman spectra.[28] However, experimental determination of the ν_1 mode of the hydrated K^+ has not yet been reported.

In this paper, we describe results of the isotropic Raman spectra for aqueous KX (X: Cl, Br, NO_3, and SCN) solutions with salt concentrations of 1–7 mol % KX observed in the frequency range of $30 \le \tilde{\nu} \le 1000\,cm^{-1}$ in order to observe the totally symmetric vibrational mode of the hydrated K^+, $K^+(H_2O)_6$. In the low-frequency region of the observed spectra, various intermolecular vibrational modes arising from the solvent–solvent, solute–solvent, and in concentrated solution, solute–solute interactions, overlap each other. Since the isotropic Raman spectra are sensitive to vibrational modes with higher symmetry, the intermolecular vibrational modes with lower symmetry such as intermolecular hydrogen-bond stretching appearing at $\tilde{\nu} \approx 180\,cm^{-1}$ in the anisotropic Raman spectra[29,30] and intermolecular bending among hydrogen-bonded water molecules ($\tilde{\nu} \approx 60\,cm^{-1}$)[29,30] disappear in the isotropic Raman spectra. Measurements of D_2O solutions with 7 mol % KCl, KBr, and KSCN solutions and 5 mol % KNO_3 solution were carried out to confirm the assignment of the observed ν_1 mode of the $K^+(H_2O)_n$ unit.

Experimental and Data Analysis

Materials. The sample solutions were prepared by dissolving weighed amounts of KCl, KBr, KNO_3, and KSCN (Nacalai Tesque Inc. Guaranteed grade) in distilled water and in D_2O (99.9% D, Aldrich Chemical Inc.). The sample solution was filtered with a 0.45 µm Teflon millipore filter before introducing it into a pyrex Raman cell ($10 \times 10\,mm^2$, 40 mmH), in order to remove dust particles.

Raman Spectroscopic Measurements. The Raman spectra were observed at 25 °C in the frequency range of $30 \le \tilde{\nu} \le 1000\,cm^{-1}$ using a JASCO NR-1100 spectrometer with a 514.5 nm line of a Spectra-Physics Stabilite 2017 Ar^+ laser operated at 200 mW. The Raman intensities were recorded at $1\,cm^{-1}$ intervals in both the parallel and perpendicular polarization modes with a spectral slit width of $5\,cm^{-1}$. Each run with a scan speed of $30\,cm^{-1}\,min^{-1}$ was repeated ten times for data accumulation. The calibration for the monochromator was made measuring neon emission lines. The alignment of the polarization filter was carefully checked by measuring the perpendicular spectral intensity of the ν_1 mode of CCl_4 in the liquid state. The efficiency of the polarization filter was determined by examining the depolarization ratio for ν_2 and ν_4 modes of CCl_4.

Data Reduction. Observed parallel and perpendicular intensities were respectively converted to reduced intensities which are proportional to the square of the change in the molecular polarizability during the vibration,[31–33]

$$I^{corrected}(\tilde{\nu}) = (\tilde{\nu}_0 - \tilde{\nu})^{-4}\tilde{\nu}[1 - \exp(-h\nu/kT)]I^{obs}(\tilde{\nu}) \quad (1)$$

where $\tilde{\nu}$ and $\tilde{\nu}_0$ denote the Stokes Raman shift and wavenumber of the incident light, respectively. The isotropic Raman intensity was obtained by

$$I^{iso}(\tilde{\nu}) = I^{//}(\tilde{\nu}) - 4/3\ \gamma I^{\perp}(\tilde{\nu}) \quad (2)$$

where $I^{//}(\tilde{\nu})$ and $I^{\perp}(\tilde{\nu})$ are the corrected parallel and perpendicular intensities, respectively. γ denotes the efficiency of the polarization filter, and $\gamma = 0.953$ was employed in the present analysis. The peak decomposition of the observed isotropic intensities was performed by using the least-squares fitting procedure by the SALS program.[34] In the present analysis, the Gaussian peak shape function with the background of the third order polynomial of $\tilde{\nu}$, was employed,

$$\Sigma[I^{iso}(\tilde{\nu}) - \Sigma G_i(\tilde{\nu}) - (A\tilde{\nu} + B\tilde{\nu}^2 + C\tilde{\nu}^3)]^2 \rightarrow \text{minimum} \quad (3)$$

where $G_i(\tilde{\nu})$ is the i-th Gaussian component. Peak position, full width at half maximum, peak height, and coefficients for the background function, A–C, were treated as independent parameters during the refinement procedure. In the preliminary analysis, it was found that at least three Gaussian components are necessary to reproduce the isotropic spectra observed for KCl and KBr solutions, while the sum of two Gaussian components could reproduce the observed spectra for KNO_3 and KSCN solutions.

Results and Discussion

The composition dependence of isotropic Raman spectra observed for KCl–H_2O solutions is represented in Figure 1. Intensity of a polarized peak centered at $\tilde{\nu} \approx 180\,cm^{-1}$ exhibits

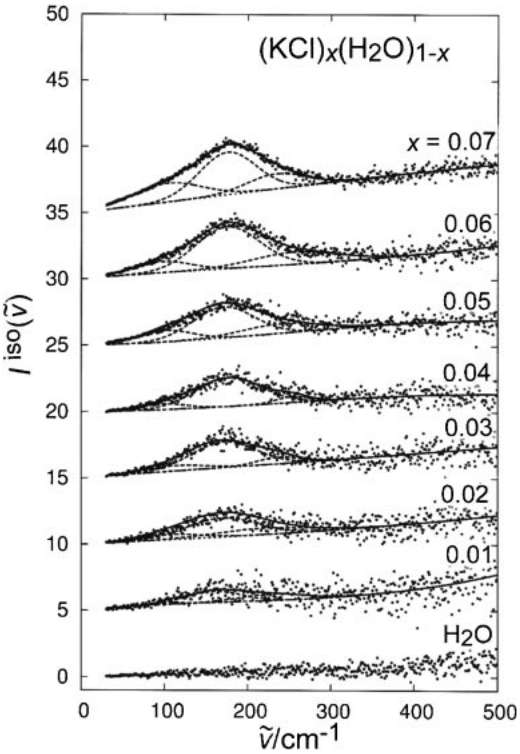

Figure 1. Composition dependence of the isotropic Raman spectra observed for aqueous KCl–H_2O solutions, $(KCl)_x(H_2O)_{1-x}$. The Gaussian components derived from the least-squares fit are indicated by broken lines.

Table 1. The Peak Position, Full Width at Half Maximum, and Peak Height of Gaussian Components Derived from the Least-Squares Fit of the Isotropic Raman Spectra for $(KX)_x(Z_2O)_{1-x}$ Solutions, $\tilde{\nu}$, w, and h, Respectively[a)]

X	x	Z	Peak 1			Peak 2			Peak 3		
			$\tilde{\nu}$/cm^{-1}	w/cm^{-1}	h	$\tilde{\nu}$/cm^{-1}	w/cm^{-1}	h	$\tilde{\nu}$/cm^{-1}	w/cm^{-1}	h
Cl	0.07	H	103(3)	96(2)	1.41(6)	175(1)	81(1)	3.20(2)	234(2)	83(5)	1.14(5)
	0.07	D	106(3)	63(10)	0.77(5)	168(1)	80(7)	2.92(1)	214(3)	86(4)	1.12(5)
	0.06	H	97(4)	79(5)	0.85(4)	175(1)	91(2)	3.15(1)	258(3)	121(10)	0.93(5)
	0.05	H	101(3)	76(3)	0.84(9)	170(1)	87(1)	2.31(3)	239(3)	109(5)	0.72(9)
	0.04	H	99(4)	64(3)	0.44(8)	177(1)	92(1)	2.16(4)	254(2)	47(10)	0.44(8)
	0.03	H	113(5)	85(4)	0.40(9)	172(1)	91(1)	1.96(4)	237(5)	59(8)	0.52(9)
	0.02	H	106(3)	86(3)	0.40(5)	169(1)	101(2)	1.45(5)	219(4)	133(4)	0.5(1)
	0.01	H	107(5)	26(8)	0.14(7)	159(1)	77(3)	0.84(9)	229(6)	92(10)	0.5(2)
Br	0.07	H	97(2)	88(6)	1.22(4)	166(1)	81(4)	4.44(2)	240(2)	91(4)	1.24(4)
	0.07	D	98(3)	72(8)	1.03(5)	155(8)	64(26)	2.96(7)	191(8)	126(10)	1.93(9)
	0.06	H	105(5)	63(5)	0.95(1)	166(1)	71(1)	3.94(1)	239(5)	83(5)	1.12(1)
	0.05	H	106(3)	69(5)	0.60(6)	166(1)	77(1)	2.52(3)	241(4)	71(6)	0.60(4)
	0.04	H	110(5)	84(8)	0.74(8)	166(1)	74(1)	1.90(4)	235(5)	89(5)	0.66(6)
	0.03	H	100(21)	111(59)	0.16(6)	160(2)	99(4)	1.58(6)	266(9)	76(22)	0.30(8)
	0.02	H	75(8)	57(6)	0.14(3)	157(1)	94(5)	1.40(6)	244(5)	73(10)	0.3(1)
	0.01	H	108(8)	63(8)	0.37(7)	156(8)	63(25)	0.92(4)	212(5)	74(9)	0.45(2)
NO_3	0.05	H	103(3)	99(5)	2.4(2)	166(2)	165(4)	2.5(1)	—	—	—
	0.05	D	94(5)	132(8)	1.7(2)	151(2)	192(2)	1.9(1)	—	—	—
SCN	0.07	H	99(3)	61(4)	0.6(1)	165(2)	104(2)	2.3(1)	—	—	—
	0.07	D	111(5)	62(5)	0.8(2)	155(2)	110(3)	2.7(1)	—	—	—

a) Estimated errors are given in parentheses.

a systematic increase with increasing KCl content, indicating that the observed polarized peak is certainly related to the intermolecular interaction between solute ions and water molecules. It should be pointed out that no intermolecular vibrational band for pure H_2O is observed in the isotropic Raman spectrum in the frequency range below 300 cm^{-1}. The present result is in accordance with the observed depolarization ratio for pure H_2O by Walrafen.[30] The isotropic Raman spectra for pure H_2O in the low-frequency region have been investigated by Brooker et al.,[24,35] in which a small polarized peak has been reported at $\tilde{\nu} \approx 180$ cm^{-1}. Considering the intermolecular hydrogen-bonded interaction modes among water molecules have been predicted to exhibit purely depolarized nature,[36] the small polarized peak observed by Brooker et al. might be caused by the imperfection in extracting the isotropic intensities by subtracting $4/3I^{\perp}(\tilde{\nu})$ from the $I^{//}(\tilde{\nu})$. The low-frequency isotropic Raman spectra for the saturated aqueous KCl solution obtained by Brooker et al.[24] indicated a polarized Raman peak at $\tilde{\nu} \approx 180$ cm^{-1} which may agree in appearance with the present data, however considerable uncertainties in their isotropic intensity might be included. The polarized peak appearing at $\tilde{\nu} \approx 180$ cm^{-1} in the present isotropic spectra can therefore be attributable to the symmetric stretching vibrational mode of the $K^+(H_2O)_6$ and/or $Cl^-(H_2O)_6$ structural units. Although considerably short residence time for hydrated K^+ (4.8 ps) and Cl^- (4.5 ps) have been estimated from the MD simulation study,[14] the present results indicate that the symmetric stretching modes of hydrated ions with short residence time can be observed in the isotropic Raman spectra.

The peak position, full width at half maximum, and peak height for the Gaussian components are given in Table 1. The assignment of the low-frequency polarized peak observed for the aqueous solutions has often been a matter of controversy. Kanno and Hiraishi have attributed the low-frequency polarized Raman peaks observed for glassy LiX and CaX_2 (X: Cl and Br) aqueous solutions to the stretching vibrational modes of hydrated halogenide ions.[37,38] Rudolph et al. assigned the low-frequency isotropic Raman peaks of $\tilde{\nu} = 190$–204 cm^{-1} and $\tilde{\nu} = 176$–191 cm^{-1} to the stretching vibrational modes of O–H···Cl$^-$ and O–H···Br$^-$, respectively.[27] On the other hand, the polarized Raman peaks at $\tilde{\nu} = 165$–192 cm^{-1} observed for $(LiBr)_x(H_2O)_{1-x}$ ($x = 0.05$–0.25) solutions have been attributed to the symmetric stretching vibrational modes of $Li^+(H_2O)_n$ ($n = 4$ and/or 6) structural units on the basis of the results of H/D and $^6Li/^7Li$ isotopic substitution experiments.[26] If the solvent H_2O molecules are replaced by D_2O, the vibrational frequency of the symmetric stretching mode, ν_1, of $M^+(H_2O)_n$ (M^+: alkali metal ion, $n = 4$ or 6) will shift to lower frequency by ca. 5%.[39] On the other hand, the O–H···X$^-$ stretching vibrational frequency might be affected more significantly on the H/D substitution because the water molecule interacts with the X$^-$ through one of the hydrogen atoms. Another question emerges from the magnitudes of the diagonal terms of the polarization tensor for the hydrated halogenide ion, $X^-(H_2O)_6$, the square sum of which is proportional to the observed Raman intensity. Even if the O–H···X$^-$ stretching mode is actually present in the solution, the polarized Raman peak should be observed only on the condition that the value of the sum of the squares of the diagonal terms of the polarization tensor should

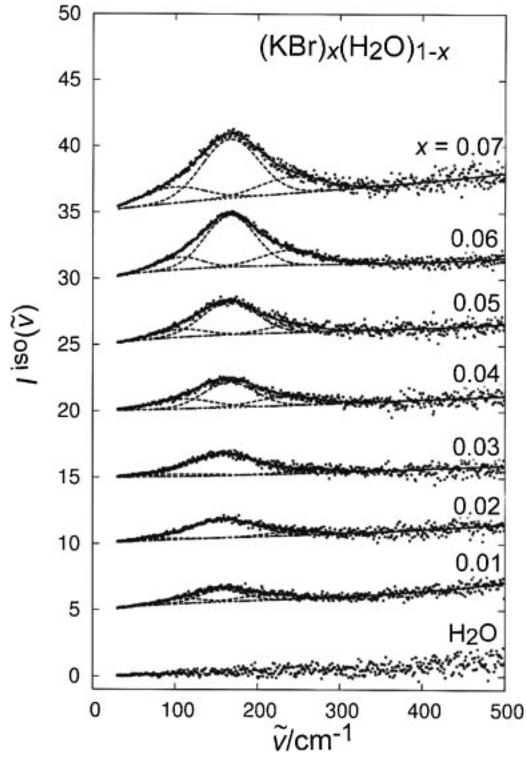

Figure 2. Same notations as in Figure 1, except for aqueous KBr–H_2O solutions, $(KBr)_x(H_2O)_{1-x}$.

not be zero. Anyway, in order to clarify the present circumstances, it is necessary to evaluate individual terms of the polarization tensor of the $X^-(H_2O)_n$ unit that is perturbed by water molecules in outer hydration shells. This requires the MD simulation combined with the ab initio molecular orbital theory involving the effect of the second or higher hydration shell. Therefore, we have to consider the anion dependence of the observed isotropic Raman spectra at present to distinguish the ν_1 mode of $K^+(H_2O)_6$.

The concentration dependence of the isotropic Raman spectra for aqueous KBr solutions is shown in Figure 2. As observed in the KCl solution, a systematic increase in the intensity of the isotropic spectra at $\tilde{\nu} \approx 170\,\mathrm{cm}^{-1}$ is evidently observed. In the present analysis, three Gaussian components were employed to fit the observed total isotropic intensities. The results of the least-squares fitting refinement are summarized in Table 1. The frequency of the main peak component (peak 2) gradually increases with increasing KBr concentration below 4 mol % KBr, while it remains almost unchanged over KBr concentration above 4 mol % KBr.

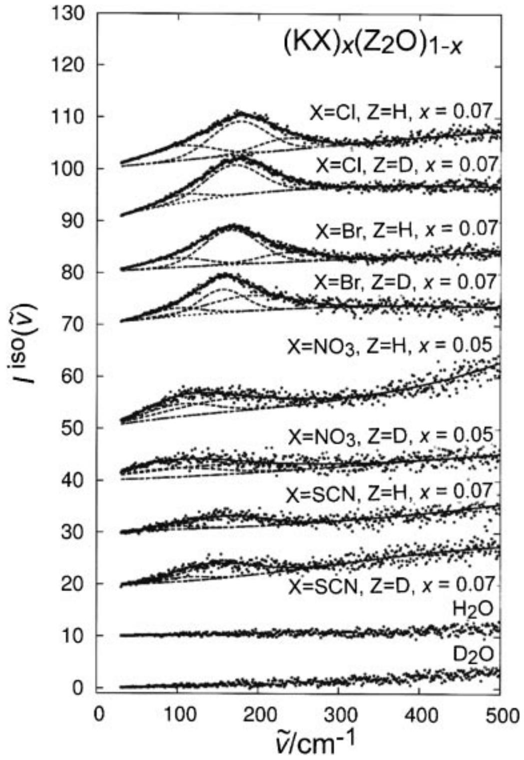

Figure 3. Isotropic Raman spectra for aqueous KX (X: Cl, Br, NO_3, and SCN) solutions in H_2O and D_2O at 25 °C. The Gaussian components derived from the least-squares fit are indicated by broken lines.

In order to obtain further information concerning the assignment of the observed polarized peak, measurements of solutions of K^+ and anions except for Cl^- and Br^- are necessary. Anions $NO_3{}^-$ and SCN^- were employed in the present study, considering the solubility of the potassium salt and different spectral features for the low-frequency isotropic Raman spectra can be expected, which should be important to distinguish the ν_1 mode of the $K^+(H_2O)_6$ structural unit. The concentration of KNO_3 and KSCN solutions were decided to be 5 and 7 mol %, respectively, considering the solubility limit of KNO_3 and to make direct comparison with the spectra for KCl and KBr solutions of the same concentration. The isotropic spectra for these solutions are represented in Figure 3. The isotropic spectrum for the KNO_3 solution exhibits asymmetric peak shape that is different from those observed for KCl and KBr solutions. On the other hand, a more symmetric isotropic peak is observed for the KSCN solution. Although the statistical uncertainties involved in these spectra are somewhat larger than those observed for the KCl and KBr solutions, peak decomposition with two Gaussian components was successfully carried out using a least-squares fit. The derived peak parameters are summarized in Table 1. The position of peak 2 was determined to be $\tilde{\nu} = 166$ and $167\,\mathrm{cm}^{-1}$ for the KNO_3 and KSCN solutions, respectively. These peak positions are in excellent agreement with that observed for the KBr solutions of the corresponding concentration. The results indicate the polarized peak observed at $\tilde{\nu} = 166$–$167\,\mathrm{cm}^{-1}$ is arising from the highly symmetric intermolecular vibrational mode of the hydrated ion that is commonly found in these solutions, i.e., $K^+(H_2O)_6$. In order to confirm the assignment of this polarized peak, measurements of the D_2O solutions were additionally carried out. The isotopic Raman spectra for the D_2O solutions are compared with those for H_2O in Figure 3. Although the overall spectra for the D_2O solutions look very similar to those observed for the corresponding H_2O solutions, the isotopic shift in the peak position of peak 2 was clearly indicated as presented in Table 1. Assuming that the present peak 2 observed in both the H_2O and D_2O solutions is attributed to the totally symmetric stretching vibrational mode of the $K^+(H_2O)_6$ and $K^+(D_2O)_6$, respectively, and the difference in the force constant for the stretching vibration between $K^+\cdots OH_2$ and $K^+\cdots OD_2$ is sufficiently small, the ratio of the vibrational frequency for the D_2O solution to that for the H_2O solution is approximately calculated by,[36]

$$\nu_{D_2O\,soln}/\nu_{H_2O\,soln} \approx (m_{H_2O}/m_{H_2O})^{1/2} = 0.95 \tag{4}$$

where m_i denotes the weight of the molecule i. It should be noted that the atomic weight of the metal ion is not involved in eq 4, which reflects that the central metal ion does not move during the totally symmetric stretching vibration of the $K^+(H_2O)_6$ structural unit. This calculated value corresponds well with the ratio $\nu_{D_2O\,soln}/\nu_{H_2O\,soln}$ for the present position of peak 2, observed for 7 mol % KCl (0.96 ± 0.01), KBr (0.93 ± 0.04), KSCN (0.94 ± 0.02), and 5 mol % KNO_3 (0.91 ± 0.02) solutions, respectively. On the other hand, the $\nu_{D_2O\,soln}/\nu_{H_2O\,soln}$ ratio for peak 1 for the KCl, KBr, KNO_3, and KSCN solutions, and the ratio for peak 3 observed in the KCl and KBr solutions, do not exhibit any systematic isotopic shift, suggesting that only peak 2 is closely related to the symmetric stretching mode in $K^+(H_2O)_6$ and $K^+(D_2O)_6$ structural units. It can be pointed out that strong anion dependence is present for the value of the full width at half maximum for peak 2. This might indicate the difference in the relative stability of the $K^+(H_2O)_6$ structural unit between these solutions.

The ν_1 frequency of the $K^+(H_2O)_6$ observed for concentrated aqueous KCl solutions is ca. $10\,cm^{-1}$ higher than that for KBr solutions. The frequency of the totally symmetric stretching mode of the $K^+(H_2O)_6$ may be influenced by the second hydration shell of the K^+ in which water molecules are hydrogen-bonded to the water molecules in the first hydration shell. In highly concentrated aqueous 7.6 mol % KCl solution, the formation of $K^+\cdots Cl^-$ contact ion pairs has been reported from the X-ray diffraction study.[4] This implies that the Cl^- could frequently be involved in the second hydration shell of K^+, which should perturb the ν_1 frequency of the $K^+(H_2O)_6$. The difference in the ν_1 frequency of $K^+(H_2O)_6$ between the KCl and KBr solutions may arise from the difference in the atomic weight between Cl^- and Br^- involved in the second hydration shell of K^+.

The origin of the lower-frequency component, peak 1, appearing at $\tilde{\nu} \approx 100\,cm^{-1}$ in the observed isotropic spectra for the KNO_3 and KSCN solutions, is not clear at present. The low-frequency component in the isotropic Raman spectra at $\tilde{\nu} \approx 135\,cm^{-1}$ was previously reported for 10 mol % $NaNO_3$ solution, in which the ν_1 mode of the hydrated Na^+, $Na^+(H_2O)_n$, was found at $\tilde{\nu} = 187\,cm^{-1}$.[28] It may be considered that this low-frequency component might be attributed to hydrated NO_3^-, however, it is necessary to investigate the intermolecular vibrational frequencies as well as components in the Raman polarizability tensor which will require further ab initio MD calculation.

In conclusion, the totally symmetric stretching vibrational mode of hydrated K^+, $K^+(H_2O)_6$, was observed at $\tilde{\nu} = 160$–$170\,cm^{-1}$ in the low-frequency isotropic Raman spectra. The present value of the ν_1 frequency is relatively lower than that observed for the hydrated Li^+ ($\tilde{\nu} = 190$–$260\,cm^{-1}$)[26,27] and Na^+ ($\tilde{\nu} = 183$–$187\,cm^{-1}$),[28] indicating that the weaker interaction between K^+ and water molecules in the first hydration shell. These results may be explained by both the order of the ionic radius which governs the electrostatic interaction between the ion and neighboring water molecule, and the strength of the electronic interaction between the alkali metal ion and water molecules in the first hydration shell.

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